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This report describes work conducted during the period 1 October 1987 through 30 April 1990, under Contract AFOSR-88-0010, "X-Ray Optics Research." Herein we describe the production of x-ray optical elements for several wavelengths by sputtering. We describe the installation of a "silicon/metals" molecular beam epitaxy (MBE) apparatus and its use in an extensive study of multilayer mirrors based on molybdenum and silicon. Continuing work on several additional materials is decribed. Finally, studies of substrate and interfacial roughness, using a scanning tunneling microscope (STM) and a WYKO phase-shifting interferometer, are presented.

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X-RAY OPTICS RESEARCH

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20 September 1990

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INTRODUCTION

During the contract period we produced high-reflectivity X-UV mirrors by sputtering, simultaneously carrying out our unique molecular beam epitaxy (MBE) program. Our "silicon/metals" MBE system arrived in March 1988 and passed its acceptance tests that June. We produced our first epitaxial, single-crystal film in July. MBE studies of film uniformity and substrate roughness were completed. Growth studies of Mo and $SiMo_x$ on Si, with emphasis on their potential use in x-ray optical elements, were also completed. In addition, multilayer mirrors for 182 Å were fabricated by MBE. We completed the first stage of a search for new material pairs that are particularly suited to MBE growth and that exhibit high reflectivity at important soft x-ray wavelengths. We began MBE growth studies on the most promising materials found. Mirrors for 125 Å, 182 Å, and 236 Å were produced by sputtering. In addition, we completed a study of the dependence of Mo/Si multilayer quality on sputtering pressure. We performed preliminary studies of substrate roughness using a scanning tunneling microscope (STM) and a WYKO interferometer. Finally, we completed significant upgrades to our computer programs for multilayer mirror design, and wrote two new programs that automatically optimize the structure for maximum reflectance.

MBE MULTILAYER FABRICATION

MBE offers unique advantages for the fabrication of x-ray multilayers. The ability to grow extremely pure crystalline layers should enable us to fabricate x-ray multilayers with smoother interfaces and exhibiting more consistent optical properties than is currently possible. Furthermore, the technique affords more precise control of layer thickness during fabrication. The new MBE system now operating in our laboratory is ideal for exploring these possibilities.

We described our MBE apparatus in detail in our last report; only a brief description of the system will be given here. The system has four ultra-high vacuum (UHV) chambers: introduction, preparation, growth, and analysis chambers. Substrates are moved from chamber to chamber by means of two perpendicular transfer rods. The pathways for the transfer rods are maintained at UHV. The growth chamber was specifically designed for epitaxial growth of Si and refractory metals. Currently it includes electron beam evaporators for six different materials and a substrate heater that will reach 1000°C. The chamber can be equipped with up to eight Knudsen cells (currently we have two). During growth, reflection high-energy electron diffraction (RHEED) can be performed on the sample surface to monitor layer growth. Low-energy electron diffraction (LEED) also is available in the growth chamber. After deposition the sample can be moved through the UHV transfer rod path into the analysis chamber. Current analytical capabilities in this chamber include Auger electron spectroscopy (AES), x-ray photo-electron spectroscopy (XPS, or ESCA), and ion scattering

spectroscopy (ISS). An ion mill is available for depth profile studies, and an 800°C substrate heater also is available for studies of interfacial reactions and interlayer mixing.

MBE growth of Mo films and of Mo/Si multilayer mirrors were studied extensively. Each of the MBE multilayers studied was made under identical conditions, except for substrate temperature, which was varied between 40°C and 300°C. The periods of all of the multilayers are nominally the same, but samples with two different layer-thickness ratios were fabricated. The multilayers were characterized with three types of x-ray diffraction (XRD); transmission electron microscopy (TEM); Rutherford backscattering spectrometry (RBS); Auger depth profiling; and soft x-ray reflectivity measurements. The TEM was performed in collaboration with A. D. Romig and C. R. Hills at Sandia National Laboratories; the soft x-ray reflectivity was measured by R. Watts at NIST (using synchrotron radiation from SURF-II); the RBS measurements were taken at the University of Arizona by J. Leavitt; and all other measurements were taken in our laboratory.

Close inspection of the TEM micrographs reveals an interfacial layer that is between Si and Mo in contrast. Interestingly, the interfacial silicide is seen only at the Mo-on-Si interface, that is, on the bottom of the Mo layer, but not at the Si-on-Mo interface. In the 40°C sample the absorber layers are almost completely composed of polycrystalline Mo. At 200°C there is 15 to 20 Å of silicide. At 250°C the absorber layers are more than half silicide, with the top of the layers again polycrystalline Mo.

This asymmetric interfacial reaction has previously been observed in sputtered Mo/Si multilayers by Petford-Long and Holloway, both of whom hypothesized that the asymmetric nature of the silicide formation was a result of the high momentum of Mo atoms in the sputtering process. However, the strong correlation observed between the substrate temperature and the thickness of the silicide indicates that it is not the energy of the depositing atoms that drives the reaction. Furthermore, because our films are evaporated, the Mo atoms have only relatively small thermal energies (~0.1 eV) when compared to possible sputtering energies (>10 eV). One explanation for the asymmetric reaction is that it arises from a surface diffusion process during growth. If Si is the dominant diffusing species, the asymmetry could arise from diffusion of Si atoms through or over the thin Mo layer as it is being formed. This diffusion should occur relatively readily when compared to diffusion into an existing thick Mo layer. This model is consistent with the substrate temperature dependence, as higher substrate temperature would cause higher Si mobility.

Additional conclusions, drawn from other characterization techniques not described in detail above, are summarized as follows. Although heating the substrate during evaporation stimulates the formation of amorphous interfacial silicide layers, this has a positive effect on mirror performance up to 200°C. The benefit may stem from the reduction in the size of the Mo crystallites, which leads to a smoother absorber layer. Mirrors with $d_{Mo} \approx 40$ Å performed much better than those with $d_{Mo} \approx$

55 Å. XRD shows that the samples with thicker Mo layers have larger Mo crystallites, so we infer that these large crystallites result in higher interface roughness. In addition, the interfacial reaction increases the thickness of the absorber layer, moving the ratio of layer thicknesses away from optimum. These observations are important for the design of future mirrors, as they cause the optimum d_{Mo} to be less than predicted by calculations.

MBE GROWTH STUDY OF Mo-Si

Our MBE instrumentation is ideally suited to the study of the growth and structure of multilayer interfaces. This capability is central to the development of future materials for multilayer x-ray optics, because their performance is limited by interface quality. In spite of the presence of a reacted layer at the Mo-Si interface, mirrors produced with the highest reflectivity to date have been Mo/Si multilayers. If, however, the reacted layer is an intrinsic property of the interface, it will be impossible to use this material pair for very short wavelengths. We completed extensive growth studies of Mo on Si to determine the detailed structure of the Mo-Si interface.

Our investigations of the Mo-Si interface were carried out by depositing Mo onto Si(100)-(2x1) and Si(111)-(7x7) surfaces in ultra-high vacuum, followed by characterization with *in situ* RHEED, LEED, AES, and XPS. Continuous growth of multiple Mo coverages on a single Si wafer was accomplished with a technique involving a moveable sample shutter. Shifts in the XPS peaks prove that the materials react at the interface. The formation of an amorphous interfacial silicide was observed at all temperatures studied--at ~50°C, 100°C, and 200°C. The composition quickly becomes Mo rich as deposition continues. Studies at T = 100°C, which focused on Mo coverage in the range $0 < d_{Mo} < 4$ Å, showed no dependence of the growth on the substrate orientation. Evidence suggests that the stoichiometry of the silicide nearest the Si substrate is approximately that of $MoSi_2$.

Figure 1 shows the Auger intensity ratio I_{Mo}/I_{Si} versus Mo coverage for experiments at T = 200°C and at T ≈ 50°C. A comparison of the experimental data and models for the various known silicides and pure Mo indicate that the interface becomes increasingly Mo rich with increasing Mo coverage. In the early stages of growth (<4 Å Mo) the ratio is independent of substrate temperature within the experimental uncertainty. As deposition continues, however, the sample grown at the lowest temperature (T ≈ 50°C) becomes more Mo rich than the higher temperature sample (T = 200°C). The steep slope in the measured intensity ratio at high coverages shows that, after a compositionally graded region, the overlayer becomes almost pure Mo.

To determine the composition gradient of the interface, a model was constructed in which the interface is made up of successive slabs of $MoSi_x$, where x may be different for each slab. The composition of each slab was adjusted to force the calculated intensity ratio to fit the experimentally

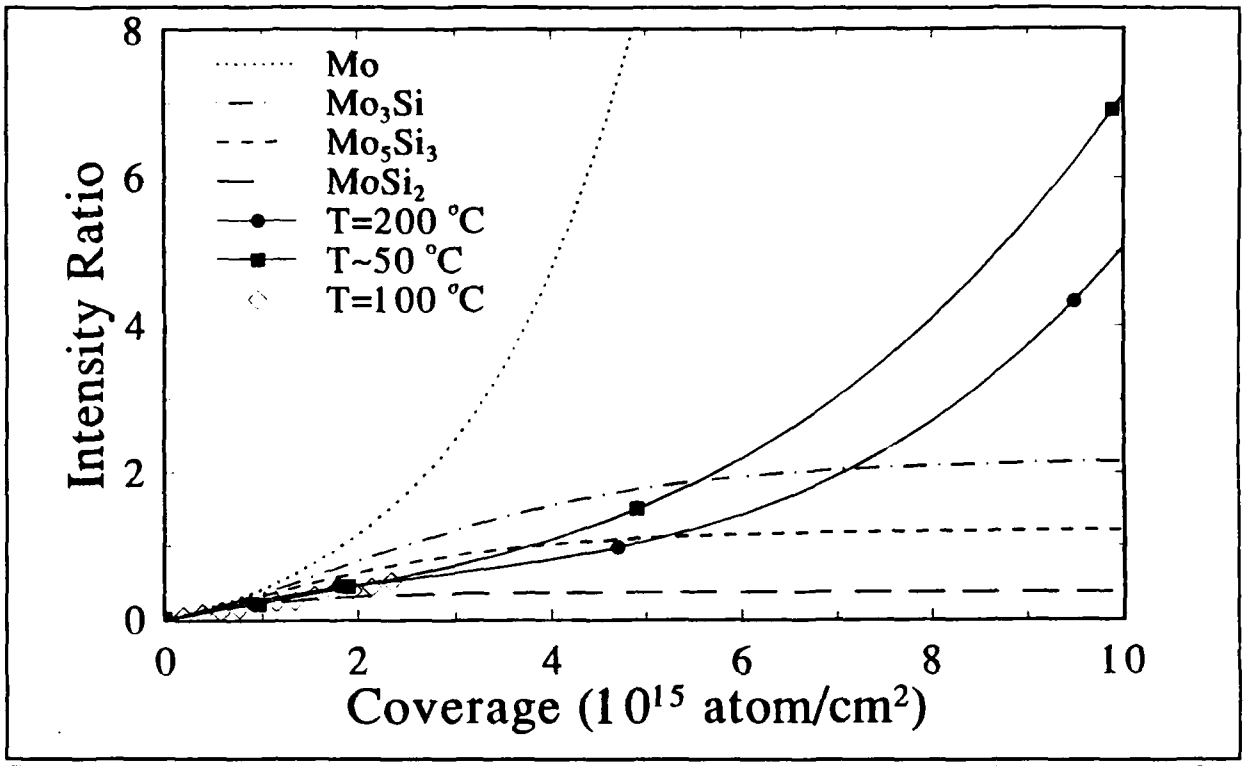

Figure 1. Auger intensity ratios for growth studies of Mo on Si(111)(7x7) at T=200 °C and T=50 °C. The dashed lines are layer growth calculations.

measured ratio at that coverage. The results of the gradient-model fits can be expressed as the atomic fraction of Mo (f_{Mo}) in each slab, as a function of the total amount of Mo deposited (coverage), or as a function of the total thickness of the overlayer up to and including that slab.

Figure 2 shows results for the gradient model for T = 200°C and T ≈ 50°C, plotted as f_{Mo} versus overlayer thickness. The error bars are larger for low coverages because, in that region, large changes in f_{Mo} result in comparatively small changes in the calculated intensity ratios. Thus, even though we have ascribed the same relative uncertainty to all of the measured intensity ratios (±10%), the uncertainty of f_{Mo} increases with decreasing coverage. Figure 2 shows that $f_{Mo}(T = 200°C) \leq f_{Mo}(T \approx 50°C)$ throughout the interface, within experimental errors, indicating the interface is broader for T = 200°C than for T ≈ 50°C. To parameterize the interface width, we fit the gradient model results with an error function of the form

$$f_{Mo} = \mathrm{erf}\left(\frac{z}{\sqrt{2}\sigma}\right) ,$$

where

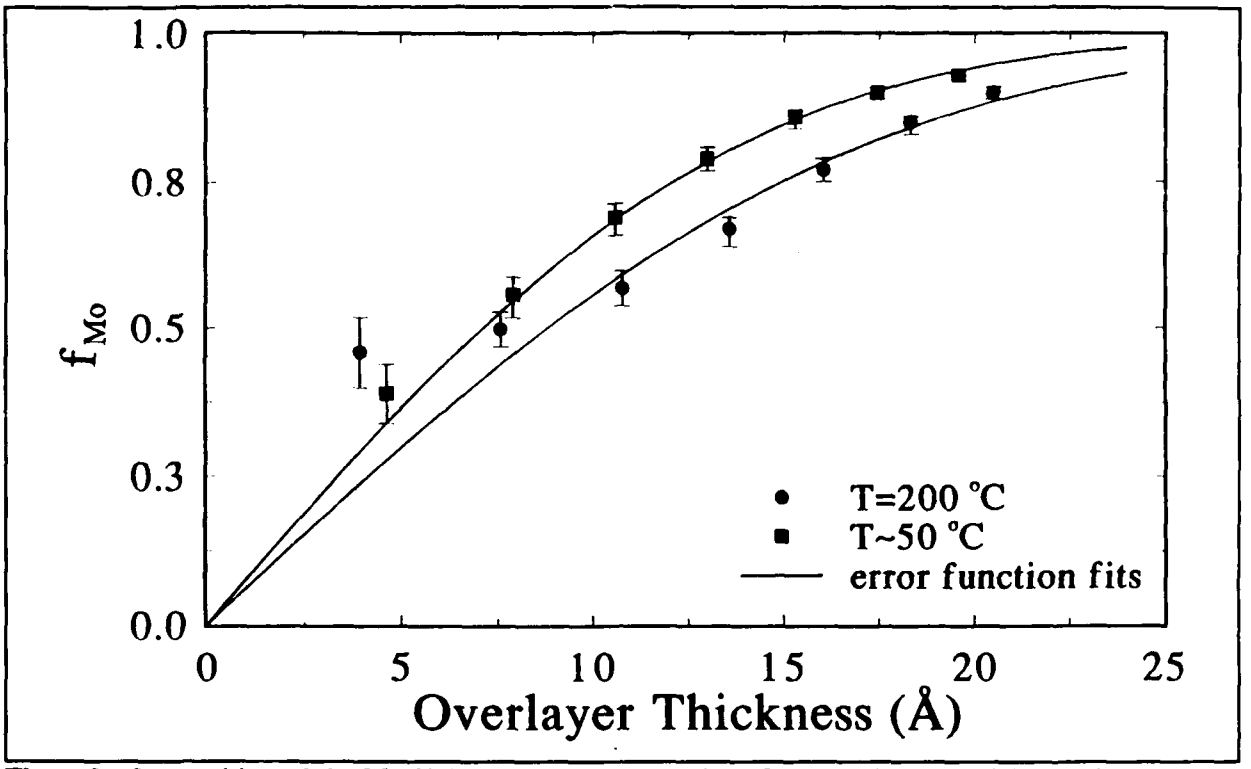

Figure 2. Composition of the Mo-Si (111) interface determined from gradient model fits to the measured intensity ratio for the samples T=200 °C and T≈50 °C.

$$\mathrm{erf}(x) = \frac{2}{\sqrt{\pi}} \int_0^x e^{-t^2}\, dt \quad .$$

Physically, this form represents diffusion at an interface located at z = 0, in which f_{Si} is unity for $z \leq 0$ and Si diffuses into the Mo for $z > 0$, creating an interface of width σ. Although the actual interface is more complicated than this simple model, resulting in a poor fit for low Mo coverage, the fit for the region of higher coverage is good enough for us to use σ as an interface width parameter. From these fits, we find σ to be 10.5 Å for T ≈ 50°C and 13 Å for T = 200°C.

The formation of interfacial silicide will degrade the performance of multilayer x-ray mirrors only slightly in the wavelengths at which they are most used--125 Å and 250 Å. The problem is not serious in this region because the interface width is much smaller than the wavelengths of interest. The problem becomes serious if such mirrors are desired for much shorter wavelengths. Even though the theoretical reflectivity of Mo/Si mirrors is reasonably high below 30 Å, formation of the interfacial silicides observed in the present work would make such mirrors useless. A method for inhibiting the reaction--or the use of a different combination of materials--is required for the short wavelength region.

NEW MATERIALS FOR MBE-GROWN MULTILAYER MIRRORS

MBE is capable of producing a variety of highly pure, epitaxial multilayer materials with well controlled interfaces. However, the conditions for MBE growth somewhat restricts the choice of materials. We initiated a search for new material pairs that are particularly suited to MBE growth and that exhibit high reflectivity at important soft x-ray wavelengths. Our material selection procedure considers such factors as chemical reactivity, thermal stability, and lattice match, as well as the maximum theoretical reflectivity. The precise deposition control and the many *in situ* characterization methods afforded by MBE allow significant control over the formation of interfaces.

In the 30 Å to 100 Å region our reflectivity-driven procedure reduces the field of possible choices to twenty-one elements. When we apply our structurally-driven procedure the list of viable elemental material pairs is restricted to very few members. Below about 37 Å, few acceptable elements were found. Structural constraints eliminate most of the elements that can achieve adequate performance without requiring a large number of layers. It may be that compound films--or films with a large number of layers--will be required for the production of high-performance periodic multilayer mirrors for wavelengths below 37 Å. For wavelengths above 37 Å, the three elemental systems exhibiting the most promise for future study are Ca/Ce, Au/B, and Ag/B. Calculated reflectivities of these systems are shown in Figure 3. In particular, the boron-based systems theoretically can achieve very high reflectivities (>50%) in the 67 Å to 110 Å region. Thus, if superlattices of Ag/B can be produced, the system should outperform both Mo/Si and W/C in the 67 Å to 110 Å wavelength region.

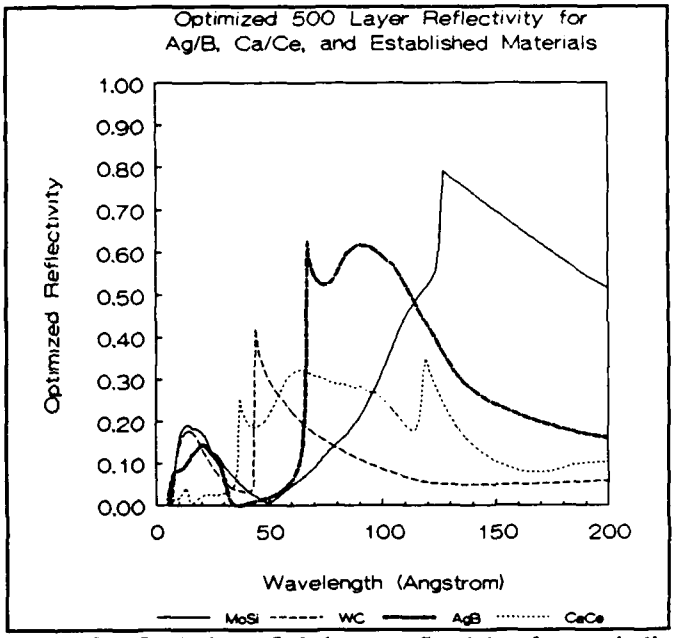

Figure 3 Optimized 500 layer reflectivity for periodic mirrors made of Mo/Si, Ag/B, W/C and Ca/Ce. Au/B is similar to Ag/B.

SPUTTERED MIRRORS

We describe in this section the major results obtained with Mo/Si multilayer optical elements produced by sputtering. We fabricated, characterized and tested a Fabry-Perot etalon designed to

work at near-normal incidence with 125-Å radiation. The etalon has a narrow intrinsic FWHM and a measured peak reflectance of 27%. Details of the etalon are contained in the previous report. Polarizing mirrors designed for 182 Å and 45° angle of incidence were fabricated, tested by our NIST collaborators at the SURF-II synchrotron, and delivered to the Princeton Plasma Physics Laboratory for x-ray laser experiments. These mirrors exhibit reflectivities between 40% and 47%, and have a uniform period across their diameter within 2%. Normal-incidence mirrors for 236 Å were also produced and delivered to collaborators at LURE, Centre Universitaire Paris-Sud, to be used as cavity mirrors in an experimental Ge-based laser. Preliminary measurements of the reflectivity of these mirrors, performed by collaborators at BESSY in Berlin, found reflectivities between 30% and 35%. Such performance is outstanding, because for this wavelength the calculated reflectivity of an ideal mirror is between 30% and 40%, depending upon the optical constants used in the calculation.

In the process of producing the mirrors described above, studies of mirror performance as a function of various sputtering parameters were performed. Our low-angle x-ray diffractometer was used to characterize the test mirrors to determine the best parameters for use in fabrication of the final mirrors. An example of a low-angle spectrum is shown in Figure 4. We have found that the

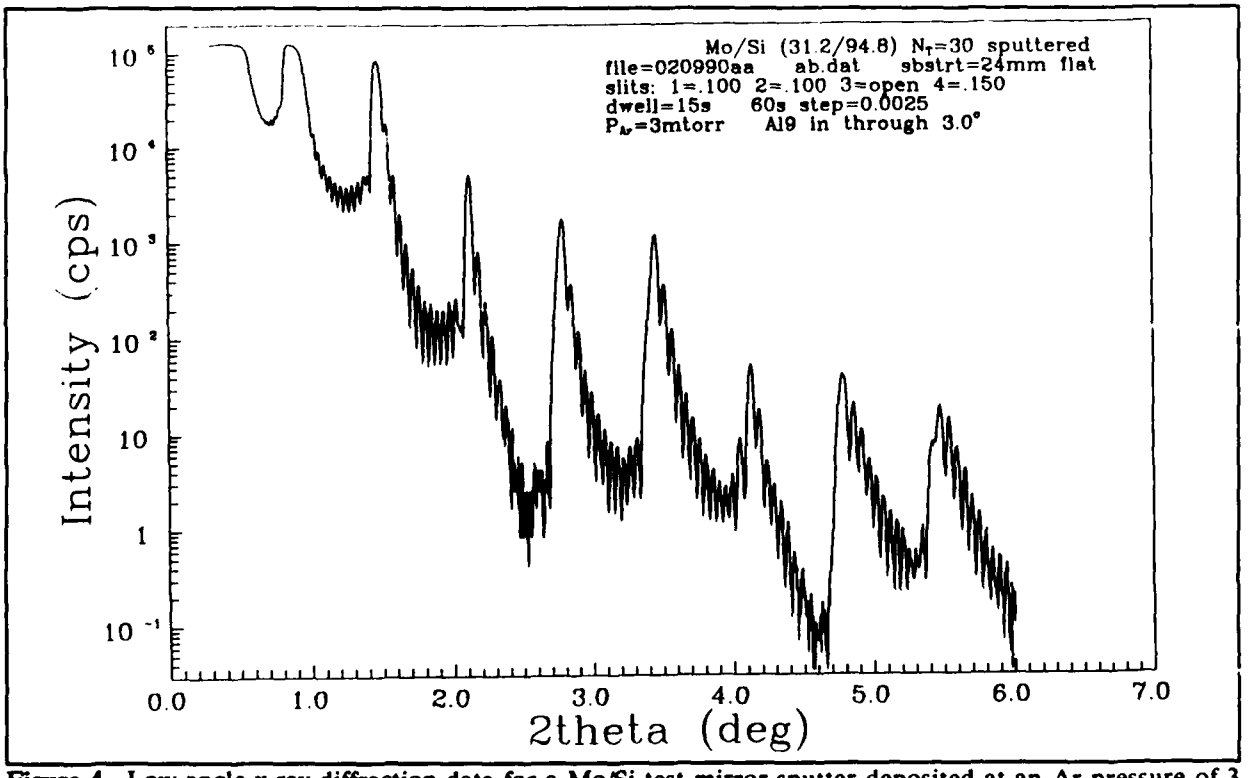

Figure 4. Low-angle x-ray diffraction data for a Mo/Si test mirror sputter deposited at an Ar pressure of 3 mtorr. The small subsidiary maxima between major Bragg peaks is a signature of reproducible layer thickness.

best parameters for Mo/Si mirrors are a sputtering pressure of 3 mtorr and a target-to-substrate distance of 12.4 cm.

SUBSTRATE ROUGHNESS

Interfacial and substrate roughness can reduce the performance of multilayer optical coatings for soft x-rays significantly. Because the wavelength of soft x-ray light is rather short, multilayers with roughness on the order of a few angstroms are required to achieve adequate performance. We took roughness measurements for uncoated silicon wafers and float glass using a WYKO TOPO-3D phase-shifting interferometer. The silicon wafers are found to be slightly smoother than the float glass samples. In addition, we examined the effects of different cleaning methods, and the effects of the deposition of silicon "buffer layers," on substrate roughness.

Si was deposited by dc triode sputtering upon candidate substrates for figured XUV optics. The substrates used in this work were float glass, semiconductor-grade silicon wafers, and diamond-turned aluminum flats. The surface-roughness profiles were measured with a WYKO TOPO-3D phase-shifting interferometer and a scanning tunneling microscope (STM). In our initial work, we observed a small step toward roughness healing in the diamond-turned aluminum with the deposition of silicon layers. Filling of microgrooves and the reduction in peak-to-valley data indicate that depositing a Si buffer layer on this substrate would improve performance of x-ray multilayer coatings. Little or no improvement in the rms roughness of the float glass and silicon wafers was seen. Additional rms measurements are needed to evaluate this method of roughness healing. We recently acquired a new STM (Nanoscope I) from Digital Instruments, Inc., that can scan over a larger range (up to 2 μm). We will be able to obtain STM data over a lateral range that overlaps the range of the WYKO interferometer.

We completed a study of Si film growth and roughness healing in our MBE system, using *in situ* RHEED and LEED. We found that, although a standard MBE acid cleaning method greatly increases the roughness of the substrates, this cleaning method is not necessary to achieve epitaxial growth of Si. To obtain a clean Si surface we first anneal the polished, semiconductor-grade Si wafer at 850°C to desorb the oxide, and then deposit a "buffer layer" of Si at 800°C to create a clean surface. We find a dramatic improvement in the surface roughness and surface crystal structure with the deposition of a buffer layer as thin as 10 Å. The improvement is particularly noticeable in the RHEED pattern, which shows a decrease in background and an improvement in the spot pattern. The final spot pattern is characteristic of a surface that is absolutely flat except for atomic steps separated by several hundred angstroms. To create the most perfect substrate surface possible, the deposition of a 100-Å Si buffer layer at 800°C has become our standard substrate pretreatment for all MBE samples.

SUMMARY

In summary, considerable advances were made under this contract. This work included: MBE studies of film uniformity and substrate roughness; growth studies of Mo and $SiMo_2$; production by MBE of mirrors for 182 Å; investigation of new material pairs for x-ray optical coatings; production by sputtering of mirrors for 124 Å, 182 Å, and 236 Å; studies of the relationship between sputtering pressure and the quality of Mo/Si multilayers; preliminary studies of substrate roughness, using our atomic resolution STM; and significant upgrades and additions to our computer codes for the design of multilayers.